ChemistrySelect

Supporting Information

Effects of Multiple OH/SH Substitution on the H-Bonding/Stability versus Aromaticity of Benzene Rings: From Computational Insights

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Author Contributions

S.P. Conceptualization:Lead; Data curation:Lead; Formal analysis:Lead; Funding acquisition:Lead; Investigation:-Lead; Methodology:Lead; Project administration:Lead; Resources:Lead; Software:Lead; Supervision:Lead; Validation:Lead; Visualization:Lead; Writing – original draft:Lead; Writing – review & editing:Lead
E.A. Writing – review & editing:Supporting

Supporting Information Summary

Table **S1**

System	B3LYP (r, ν) (in Å, cm^{-1})	MP2 (r, ν) (in Å, cm^{-1})
1a	O-H(**R**): (0.968, 3778.8)	O-H(**R**): (0.971, 3762.8)
1b	O-H(**R**): 0.965, (sym: 3819.7, antisym: 3818.6)	O-H(**R**): 0.968, (sym: 3803.4, antisym: 3803.8)
2a	S-H(**R**): 1.359, (sym: 2635.8, antisym: 2632)	S-H(**R**): (1.355, 2702.2)
2b	S-H(**R**): 1.355, (sym: 2680.3, antisym: 2680.6)	S-H(**R**): 1.351, (sym: 2741.2, antisym: 2742.6)
3a	O-H(**R**): 0.974, 3644	O-H(**R**): 0.976, 3653.3
3b	S-H(**M**): 1.354, 2696	S-H(**L**): 1.350, 2756.4
3c	O-H(**R**): 0.965, 3821.6; S-H(**M**): 1.356, 2675.1	O-H(**R**): 0.968, 3803.2; S-H(**M**): 1.351, 2741.7
4a	O-H(**L**): 0.968, 3833.3; O-H(**M**): 0.971, 3792; O-H(**R**): 0.972, 3775.6	O-H(**L**): 0.968, 3818.8; O-H(**M**): 0.971, 3768.6; O-H(**R**): 0.972, 3759
4b	O-H(**L**): 0.964, 3835.3; O-H(**M**): 0.971, 3739.2; O-H(**R**): 0.965, 3821.8	O-H(**L**): 0.967, 3820.2; O-H(**M**): 0.970, 3782.6; O-H(**R**): 0.968, 3806.3
5a	S-H(**L**): 1.360, 2627.5; S-H(**M**): 1.360, 2611.2; S-H(**R**):1.359, 2631.4	S-H(**L**): 1.355, 2699.8; S-H(**M**): 1.356, 2979.6; S-H(**R**):1.354, 2705.3
5b	S-H(**L**): 1.358, 2632.9; S-H(**M**): 1.360, 2627.8; S-H(**R**):1.357, 2652.1	S-H(**L**): 1.354, 2708.9; S-H(**M**): 1.355, 2696.7; S-H(**R**):1.352, 2734.7
5c	S-H(**L**): 1.358, (sym: 2648.3, antisym: 2646.6); S-H(**M**): 1.360, 2631.5; S-H(**R**):1.358, (sym: 2648.3, antisym: 2646.6)	S-H(**L**): 1.352 (sym: 2731.5, antisym: 2730.6); S-H(**M**): 1.355, 2701.5; S-H(**R**):1.352, (sym: 2731.5, antisym: 2730.6)
6a	S-H(**L**): 1.354, 2690; O-H(**M**): 0.970, 3751.1; O-H(**R**):0.964, 3831.8	S-H(**L**): 1.350, 2750.7; O-H(**M**): 0.967, 3819.8; O-H(**R**):0.968, 3817
6b	S-H(**L**): 1.361, 2621.3; O-H(**M**): 0.974, 3648; O-H(**R**):0.968, 3774.9	S-H(**L**): 1.355, 2707.2; O-H(**M**): 0.977, 3647.5; O-H(**R**):0.972, 3755.6
6c	S-H(**L**): 1.356, 2676.3; O-H(**M**): 0.968, 3780; O-H(**R**):0.964, 3832.4	S-H(**L**): 1.351; 2742.9; O-H(**M**): 0.972, 3756; O-H(**R**): 0.968, 3816.6
7a	O-H(**L**): 0.965, 3823.3; S-H(**M**): 1.354, 2692.4; O-H(**R**):0.965, 3822.4	O-H(**L**): 0.968, 3805.7; S-H(**M**): 1.351, 2751.6; O-H(**R**):0.968, 3803.4
7b	O-H(**L**): 0.965, 3813.6; S-H(**M**): 1.360, 2620.7; O-H(**R**):0.975, 3623.7	O-H(**L**): 0.969, 3800; S-H(**M**): 1.354, 2713.8; O-H(**R**):0.977, 3642.6
7c	O-H(**L**): 0.975, (sym: 3686.2, antisym:3677.8); S-H(**M**): 1.357, 2692; O-H(**R**):0.975, (sym: 3686.2, antisym:3677.8)	O-H(**L**): 0.972; (sym: 3685.1, antisym:3675.2; S-H(**M**): 1.363, 2600.1; O-H(**R**): 0.972, (sym: 3685.1, antisym: 3675.2)

Table **S1** Continued…….

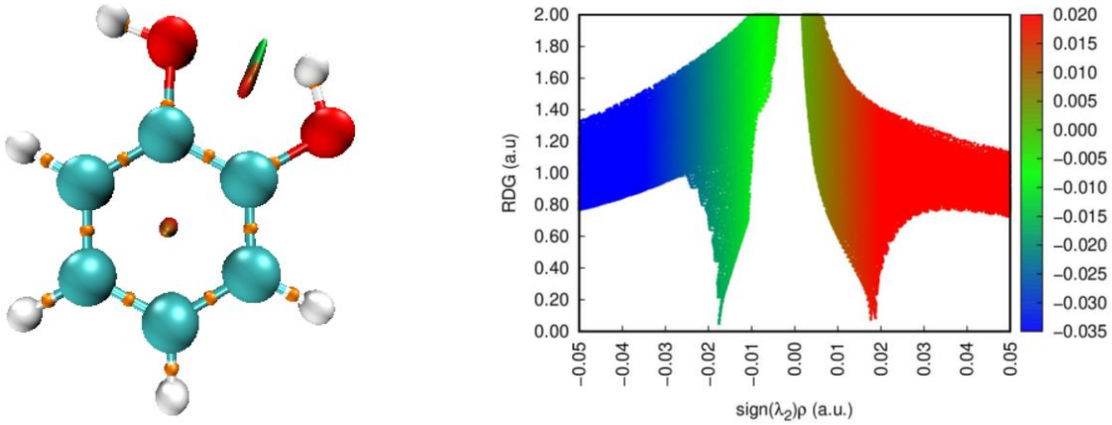
System	B3LYP (r, ν) (in Å, cm^{-1})	MP2 (r, ν) (in Å, cm^{-1})
8a	O-H(**L**): 0.974, 3635.9; S-H(**M**): 1.362, 2615.6; S-H(**R**): 1.357, 2662.4	O-H(**L**): 0.977, 3646.4; S-H(**M**): 1.356, 2701.2; S-H(**R**): 1.352, 2731.8
8b	O-H(**L**): 0.965, 3819.4; S-H(**M**): 1.354, 2680.4; S-H(**R**): 1.359, 2633.2	O-H(**L**): 0.969, 3800.6; S-H(**M**): 1.351, 2743.9; S-H(**R**): 1.355, 2703.5
8c	O-H(**L**): 0.965, 3821.6; S-H(**M**): 1.353, 2696.9; S-H(**R**): 1.355, 2679.1	O-H(**L**): 0.968, 3801.8; S-H(**M**): 1.350, 2751.1; S-H(**R**): 1.350, 2744.9
8d	O-H(**L**): 0.965, 3820.3; S-H(**M**): 1.360, 2635.2; S-H(**R**): 1.355, 2678.9	O-H(**L**): 0.969, 3800.3; S-H(**M**): 1.355, 2694.6; S-H(**R**): 1.355, 2701.3
8e	O-H(**L**): 0.974, 3648; S-H(**M**): 1.362, 2609.6; S-H(**R**): 1.359, 2634.7	O-H(**L**): 0.976, 3655.1; S-H(**M**): 1.356, 2697.8; S-H(**R**): 1.353, 2715
9a	S-H(**L**): 1.354, 2695.1;O-H(**M**): 0.975, 3617.6;S-H(**R**): 1.361, 2618.5	S-H(**L**): 1.350, 2753.8;O-H(**M**): 0.978, 3618.3;S-H(**R**): 1.355, 2706.4
9b	S-H(**L**): 1.356, 2671;O-H(**M**): 0.975, 3634.5;S-H(**R**): 1.361, 2618.5	S-H(**L**): 1.351, 2740;O-H(**M**): 0.977, 3640.2;S-H(**R**):1.355, 2707
10a	S-H **LU**: 1.360, 2606.5; **LD**: 1.361, 2597.7; **RU**: 1.361, 2596.2 Mixed S-H stretching vibrations: 2596.2, 2597.7, 2606.5, 2614.8, 2624.5, 2632.8	S-H **LU**: 1.359; **LD**: 1.358; **RU**: 1.358; **RD**: 1.359 Mixed S-H stretching vibrations: 2680.2, 2682.3, 2685.2, 2693, 2697.2, 2699.2
10b	S-H **LU**: 1.359 **LD**: 1.358; **RU**: 1.358; **RD**: 1.359 Mixed S-H stretching vibrations: 2614.3, 2615.5, 2633.7, 2636.7, 2639.8, 2641.2	S-H **LU**: 1.355, ; **LD**: 1.355, ; **RU**: 1.355, ; **RD**: 1.355 Mixed S-H stretching vibrations: 2685.4, 2687.3, 2697.4, 2700.5, 2703.2, 2704.6

NCI-RDG Isosurface Plots

Identification and graphical envision of noncovalent interactions (NCIs) regions along with the nature and strength involved therein, have been basically produced by means of the NCI-reduced density gradient (NCI-RDG) approach, which allows an inclusive description of hydrogen bonds (HBs), van der Waals (vdW) interactions, and steric repulsion in all species. Generally, localized blue lentils show the strong attractive interactions (*i.e.* HBs), thin and delocalized green regions characterize the vdW interactions, and red isosurfaces reveal the steric clashes (for example: see Figure **1a,** right side figure). The electron density (ED) and its derivatives allowing synchronized analysis and visualization of a broad range of NCIs types as real space surfaces and playing a keyrole to a chemist's arsenal, we havemade effortsin giving outline for the H-bonded species.

The RDG isosurface displayed on horizontal axis is 0.5 (ranging from -0.05 to +0.05). The Ω(r) values ranging from -0.035 atomic unit (au) to +0.02 au on vertical axis (right side) show the colored surfaces of the species on a blue-green-red scale. The detailed description of the NCI tool clarifies that the higher density values (Ω(r) < 0) show the stronger attractive interactions while the very low-density values (Ω(r) > 0) indicate the repulsive interactions. Moreover, for example, in the case of H-bonded **1a** system, blue-green mixed color spike (values lying between -0.015 and -0.02*i.e.* very close to -0.02) in the scatter map (2D plot) as well as green colored disc-shaped NCI isosurfaces (3D representation) between two atoms O (proton acceptor) and H, signifying the attractive interactiongive a clear indication of presence of HBs (O-H···O) (attractive interaction) which is also supported by the QTAIM ED based topological parameters (alteration in the rho value of the H-bonded O-H and its free form). The presence of steric effect is evidently shown by the low-gradient spikes appearing at positive side (+0.015 to +0.02)(see Figure **1a**, right side figure). This effect as shown by the red ellipsoid depicts the electron density depletion which is because of the electrostatic repulsion.

3D isosurface plot **2D color filled scatter plot**



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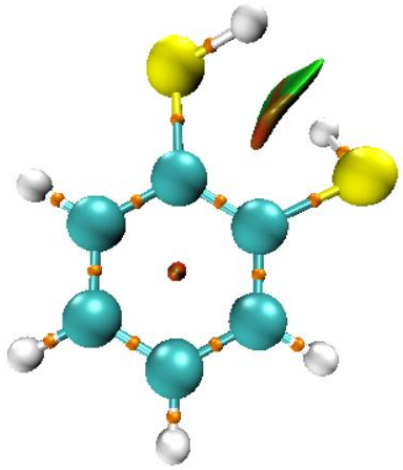
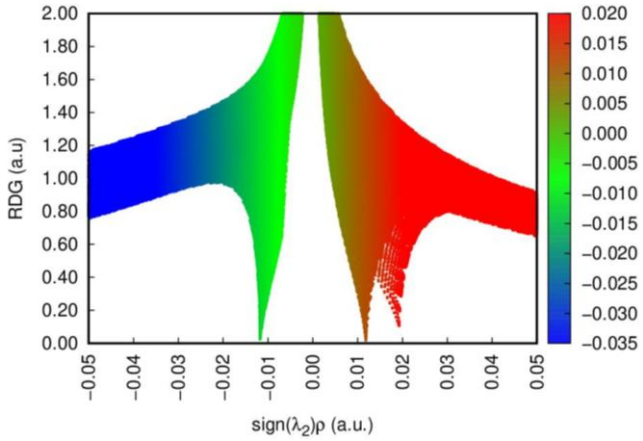
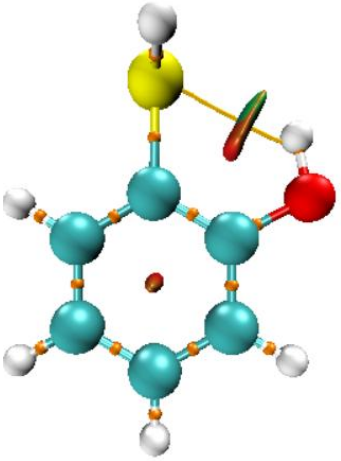
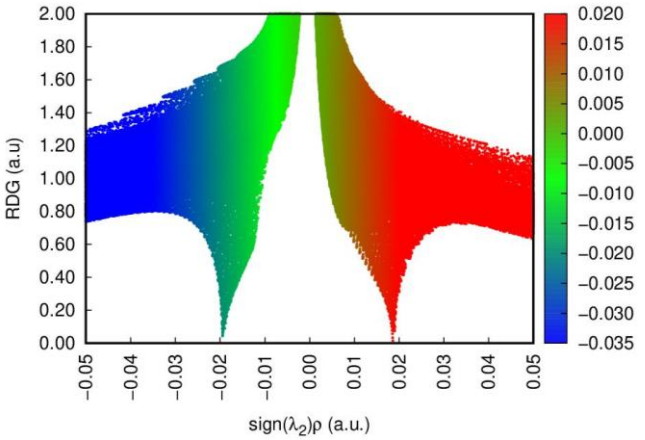


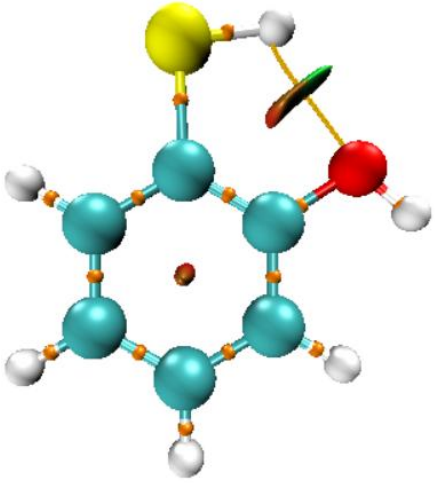


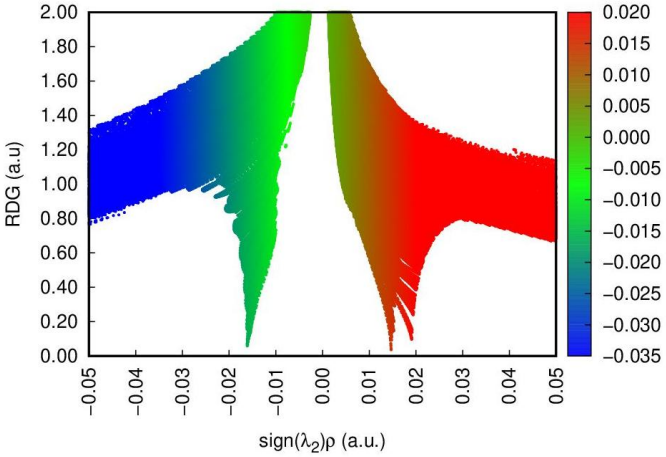
2a



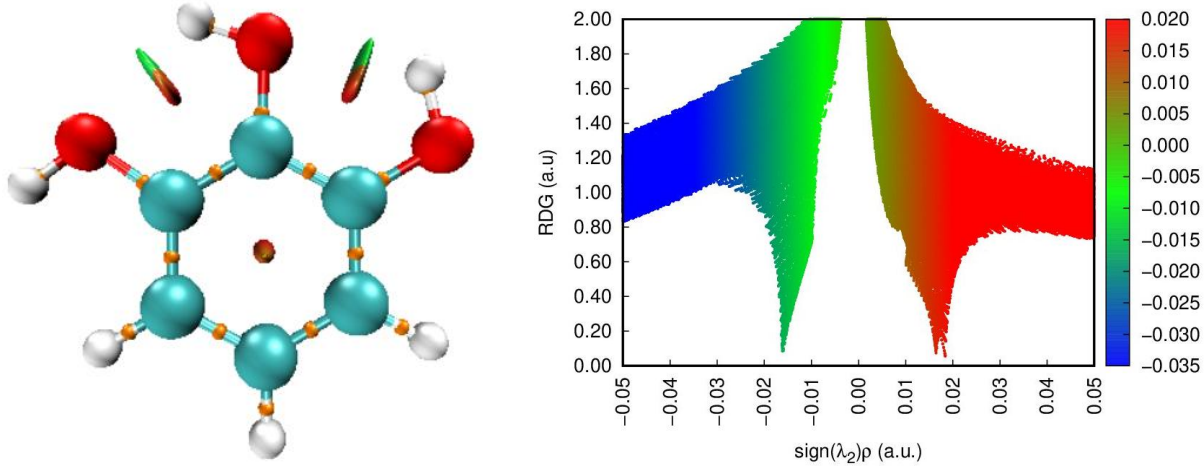


3a

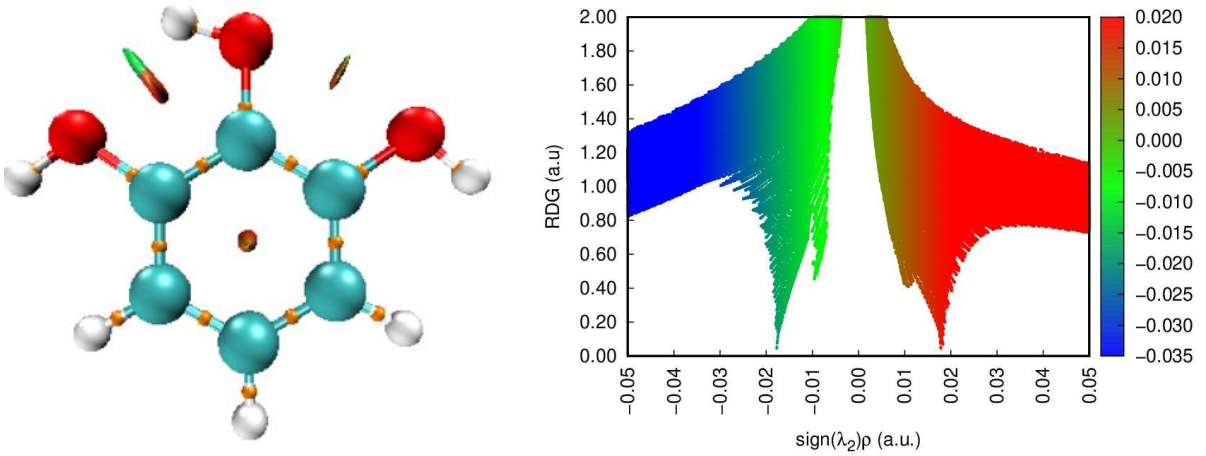




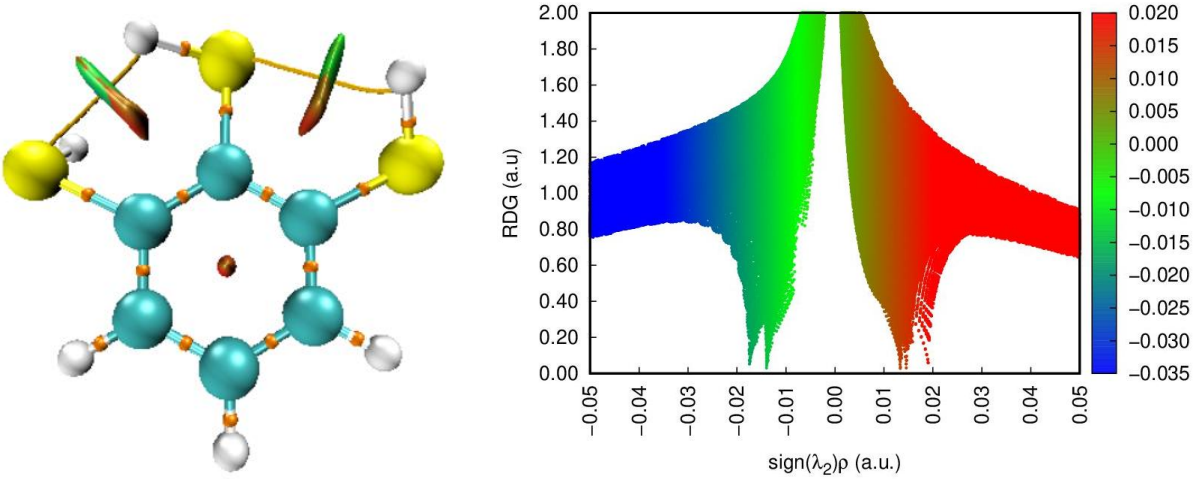
3b



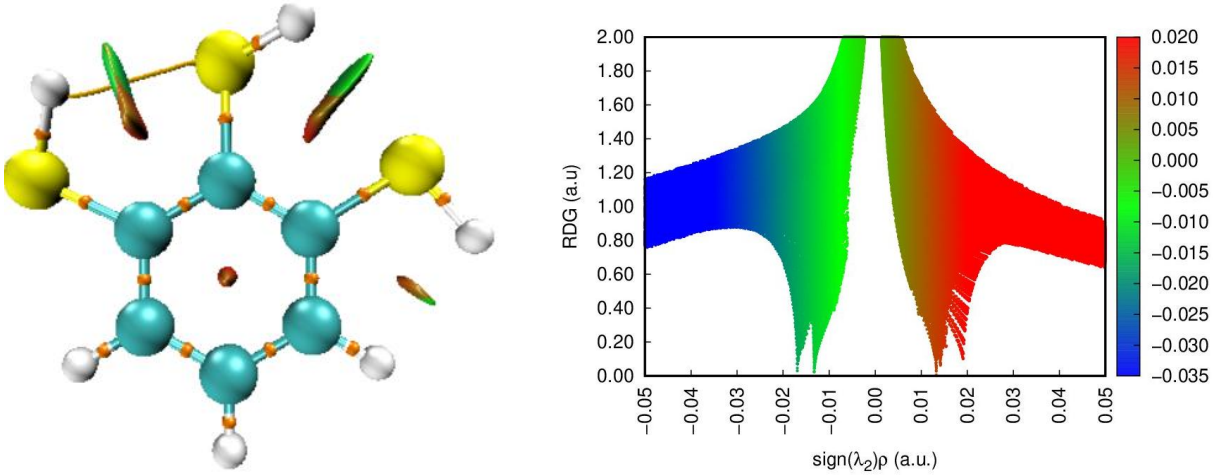
4a



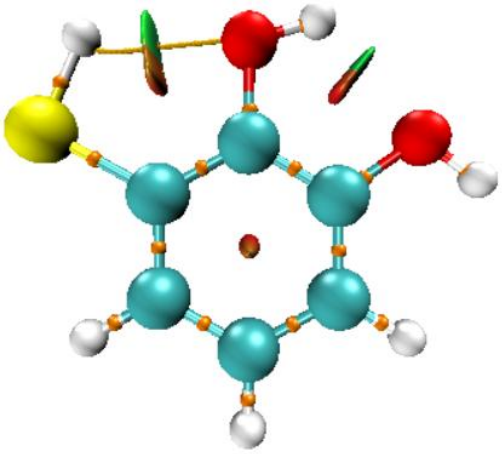
4b

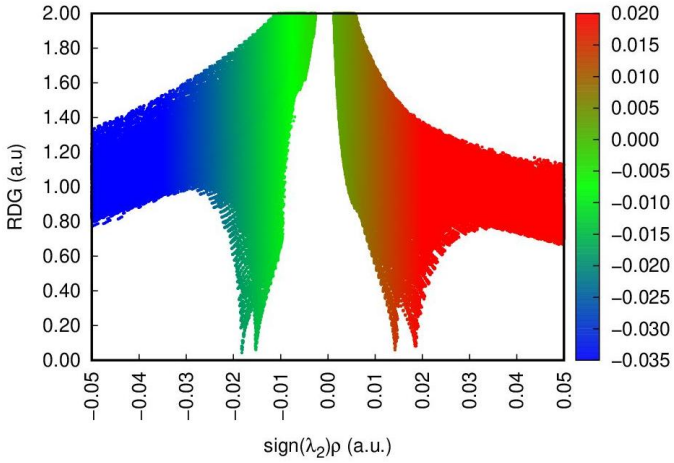


5a

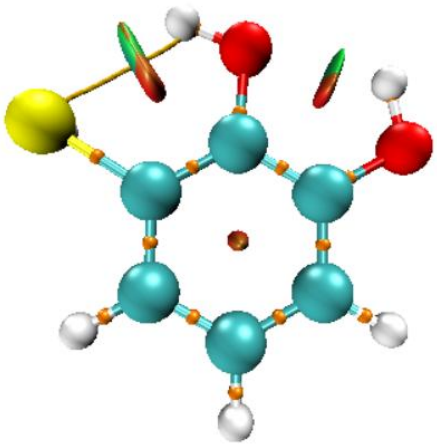


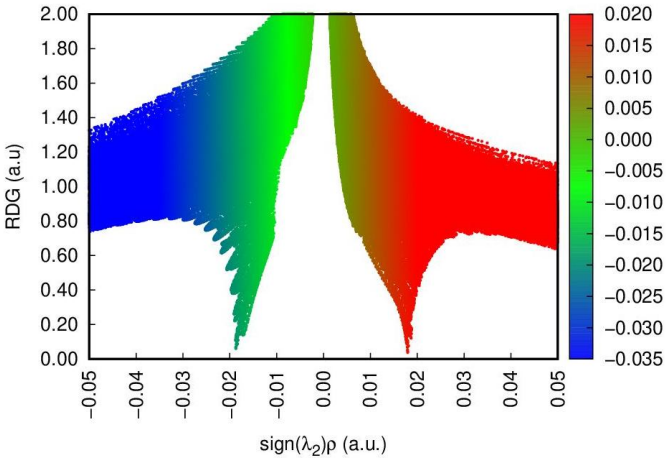
5b



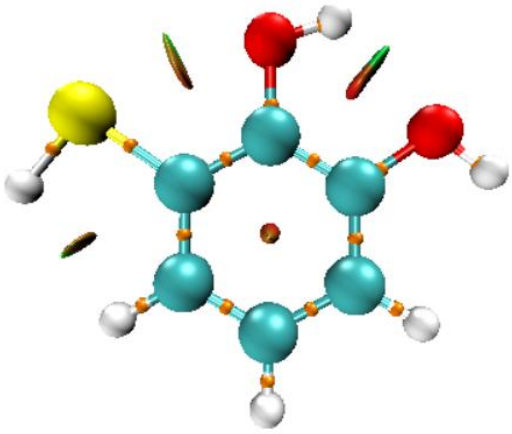


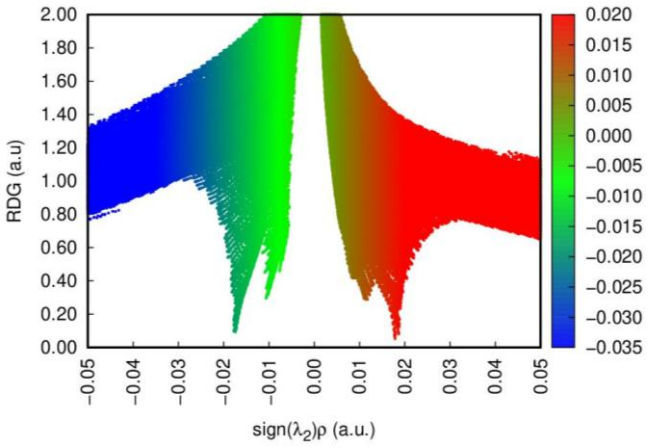
6a





6b





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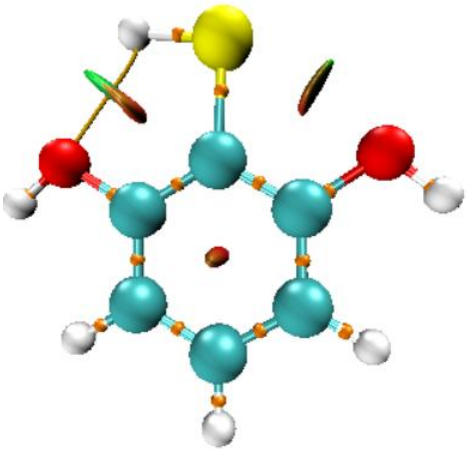

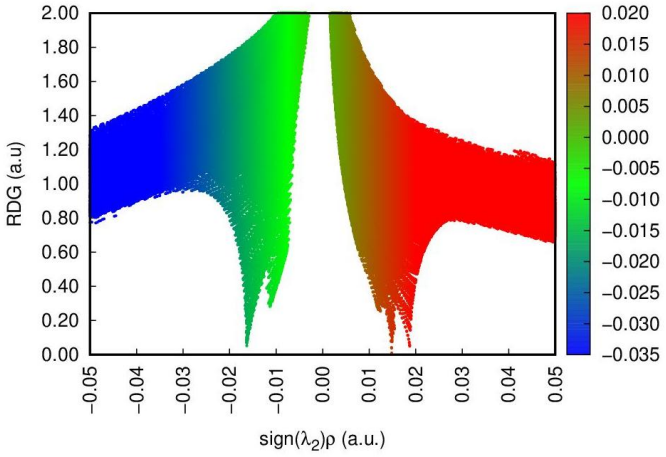

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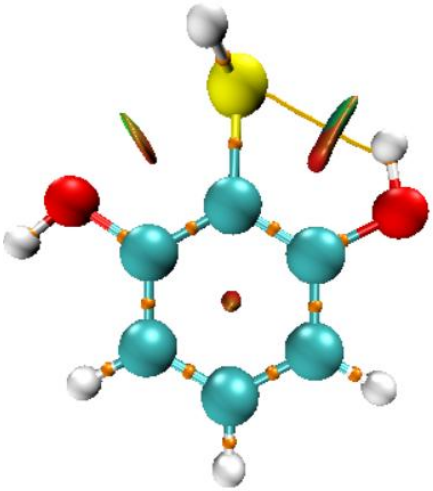

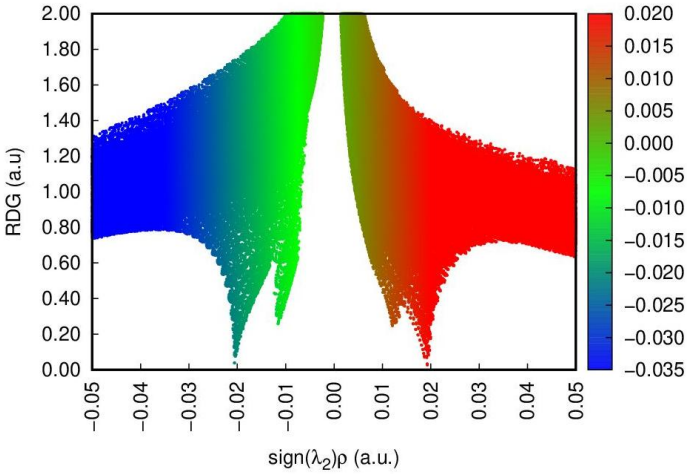

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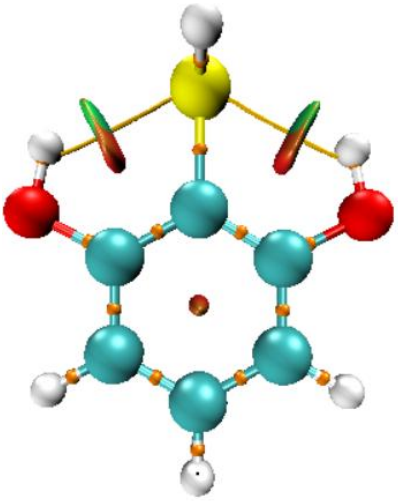

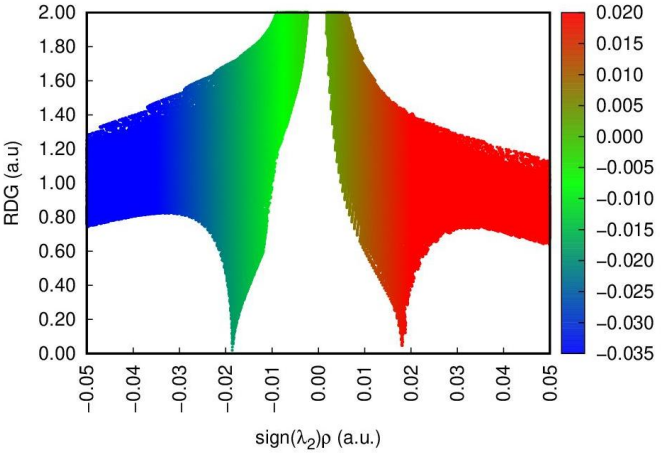

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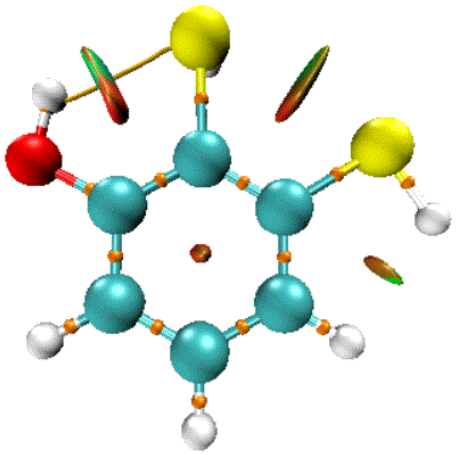

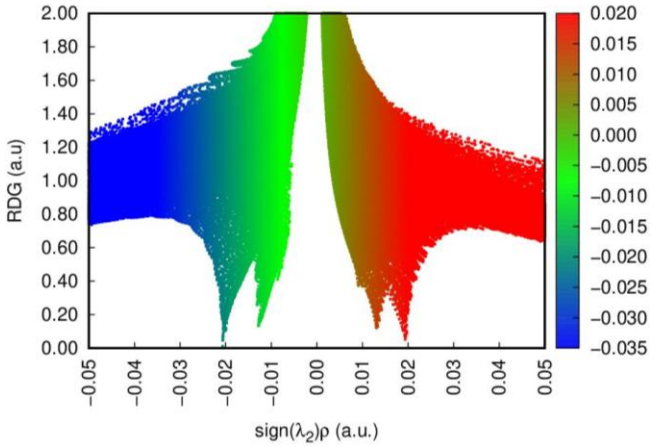

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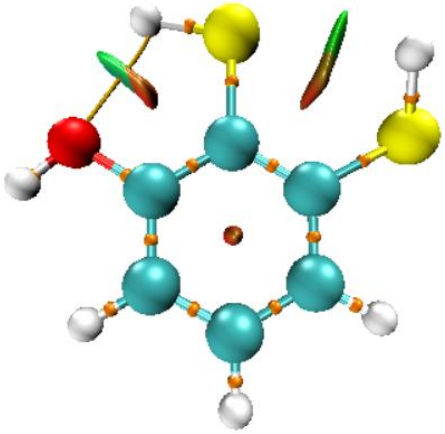

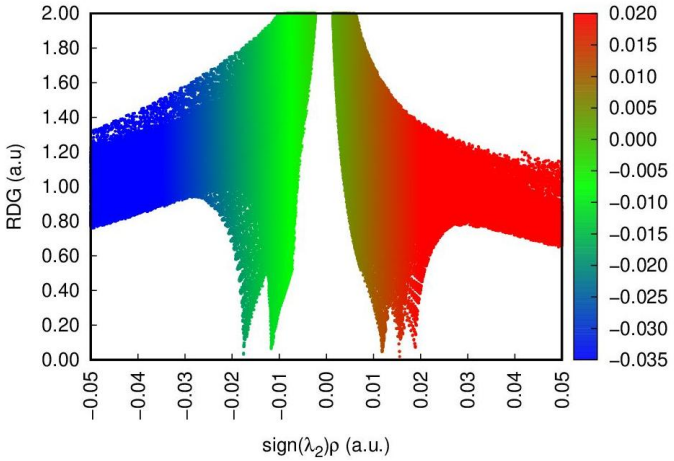

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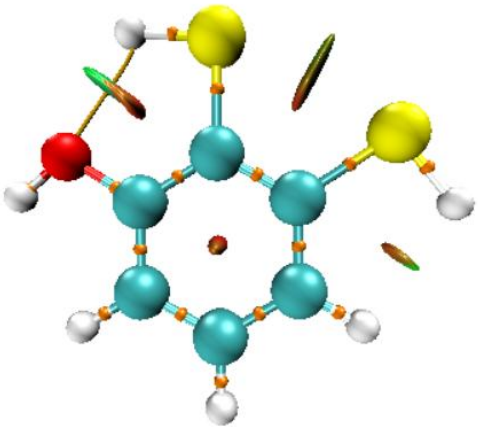

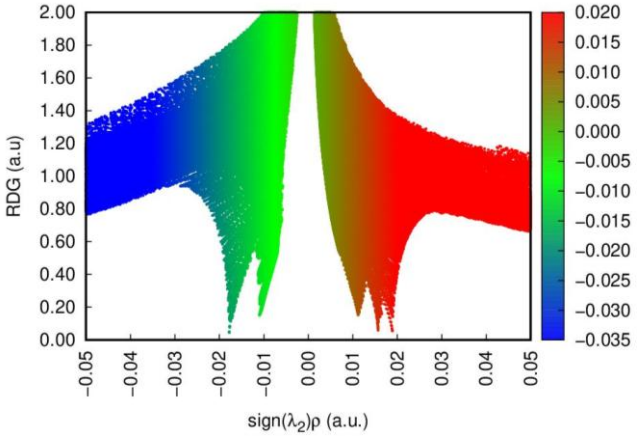

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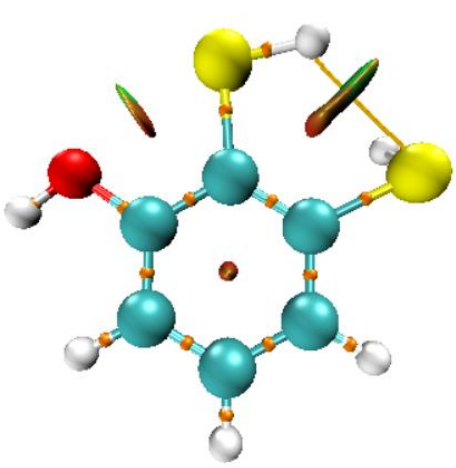
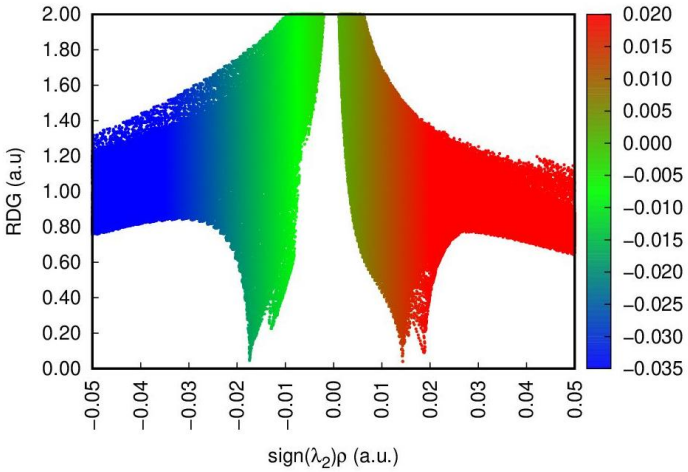
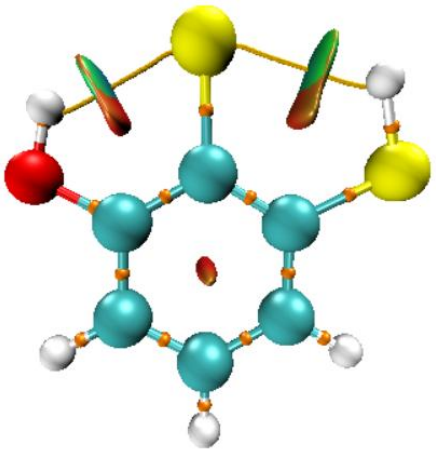
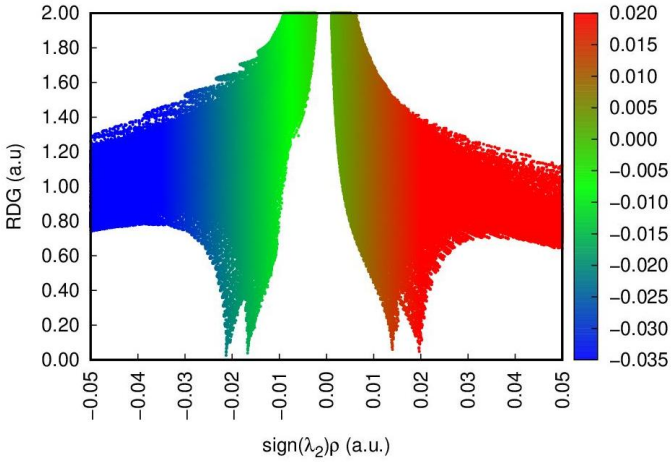


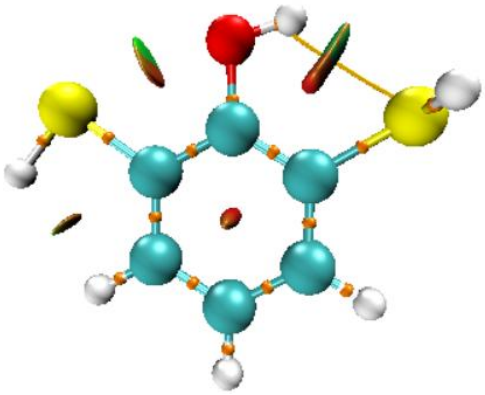

RDG (a.u)
sign(λ2)ρ (a.u.)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

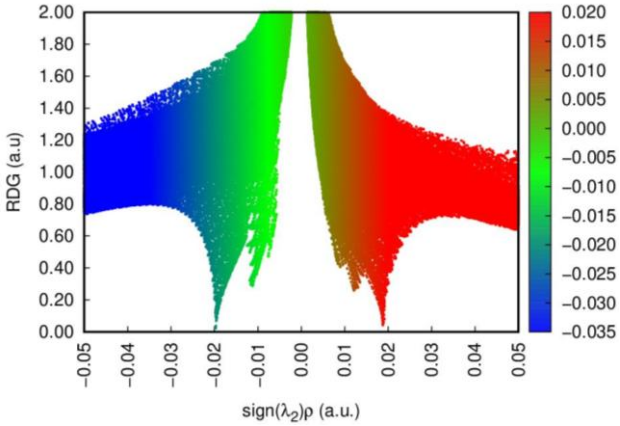
8d



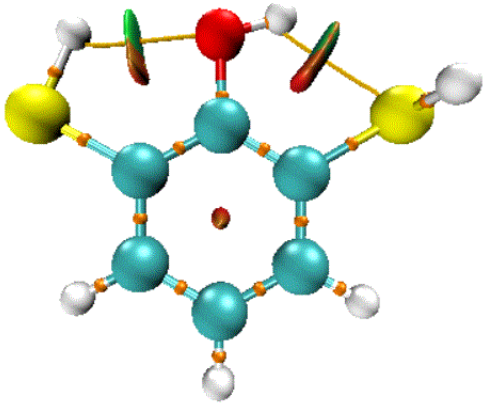

RDG (a.u)
sign(λ2)ρ (a.u.)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

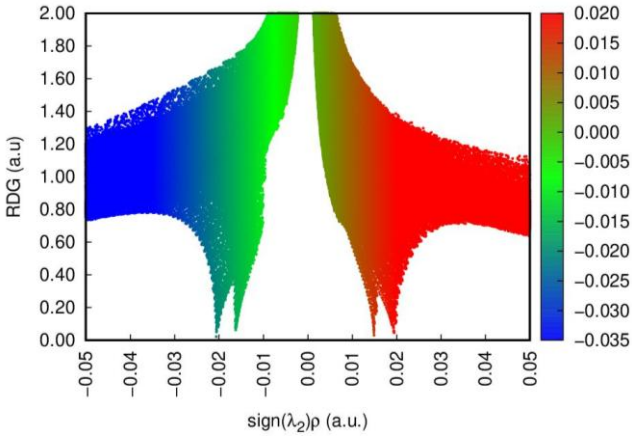
8e



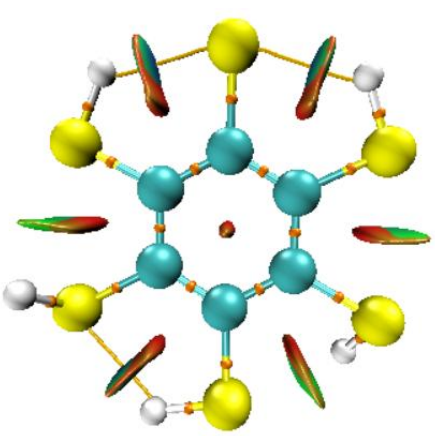

RDG (a.u)
sign(λ2)ρ (a.u.)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

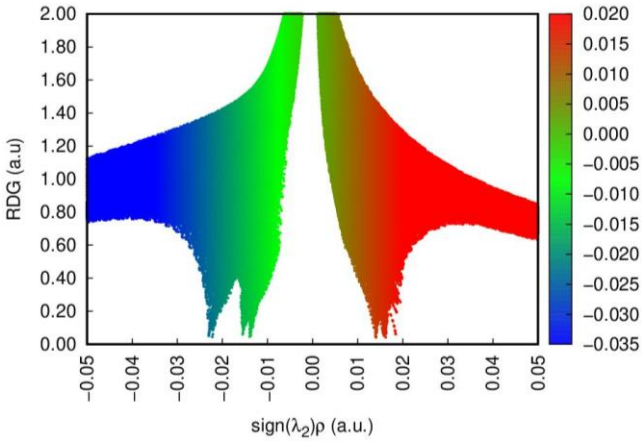
9a



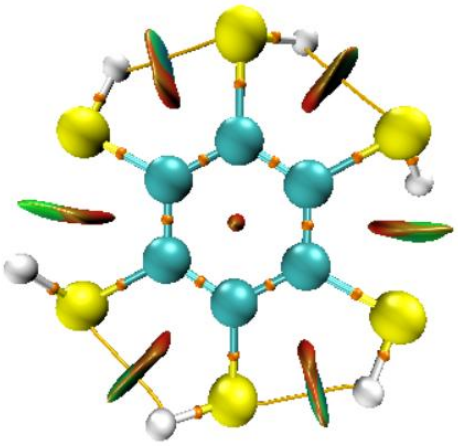

RDG (a.u)
sign(λ2)ρ (a.u.)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

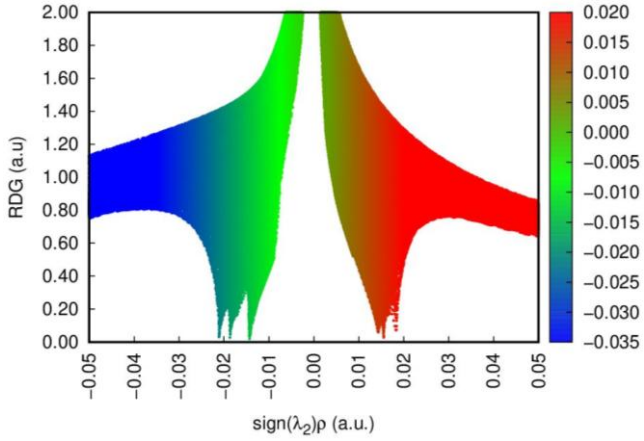
9b




RDG (a.u)
sign(λ2)ρ (a.u.)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

10a




RDG (a.u)
sign(λ2)ρ (a.u.)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

10b